

Molecular features of fossil organic matter in remains of the Lower Cretaceous fern *Weichselia reticulata* from Przenosza basement (Poland)

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Abstract

Przenosza (Western Carpathians, Poland) is an important palaeobotanical Cretaceous basement with morphologically well-preserved plant remains. Both the morphology of the macroremains and the microscopic examination of isolated plant cuticles correspond to typical species of coastal swampy palaeoenvironments, mainly the fern *Weichselia reticulata* (Stokes & Webb). After isolation of the plant remains, the preliminary characterisation of the fossil organic matter was carried out by cross polarization, magic angle spinning (CP-MAS) ¹³C nuclear magnetic resonance (¹³C NMR) spectroscopy and Curie-point analytical pyrolysis.

The ¹³C NMR suggested a III-type kerogen from predominantly terrestrial material subjected to intense dia- and catagenetic transformations. The prominent signal ~130 ppm, indicates C- or H-substituted aromatic structures, and the weak shoulder ~153

ppm suggests the removal of oxygen-containing groups from lignin and carbohydrate. The alkyl carbon signal (~30 ppm) represents about a quarter of the total ^{13}C signal intensity, suggesting an appreciable domain of selectively preserved aliphatic macromolecular structures.

Curie-point pyrolysis released major series of substituted aromatic compounds namely benzenes, phenols, naphthalenes, anthracenes/phenanthrenes, fluorenes and pyrenes (probably derived from heavily altered aromatic biomacromolecules such as lignin or tannins, or from secondary aromatisation of diagenetic structures). Typical alkyl series consisting of triplets of *n*-alkanes, *n*-alkenes, and α,ω -alkadienes were also major pyrolysis products. Methoxyphenols, catechols, fatty acids, steroids, diterpenes and sesquiterpenes were not detected or only in trace amounts. The alkyl series (including doublets of alkenes and alkadienes in the $\text{C}_6\text{--C}_{24}$ range with carbon preference index close to the unity) are similar to those found in thermally altered cutans. As opposed to the alkyl compound assemblages, the lack of indicators for selectively preserved lignin, carbohydrate or protein, points to an extensive rearrangement of phenolic constituents into a largely newly-formed condensed backbone, where the original lignin, waxes and carbohydrate have been removed or incorporated into a condensed kerogen matrix affected by severe reduction, aromatization and additional cross-linking reactions.

Keywords: Molecular palaeontology; Ferns; Curie point pyrolysis; Nuclear magnetic resonance

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1. Introduction

The Przenosza basement is located at the North of the Tatra Mountains (Poland), occupying a wide Cretaceous area of sediments at both sides of the frontier with Slovakia (Fig. 1). The basement is mainly composed of dark coloured shales including calcium carbonates and frequent pyrites. The rocks contain appreciable amounts of plant remains, but most of them are small-size fragments. The macroscopic descriptions of the morphologically well-preserved plant remains correspond to *Weichselia reticulata* (Stokes & Webb) Fontaine emend. and *Frenelopsis* sp. and were described in detail by Reymanówna (1965).

The matoniaceous fern *W. reticulata* is a typical plant of estuarine tropical or near tropical conditions and represents an early Cretaceous mangrove. It was the most abundant and characteristic tree fern at the shore of the Tethys Sea and the primitive Atlantic Ocean during the Lower Cretaceous (Reymanówna, 1965). In the Northern Hemisphere, it was widespread from North America to Japan and in the Southern from Peru to India. Its remains are known from the Upper Jurassic to the Late Cretaceous. Morphologically this plant is characterised by having thick stems (known as Paradoxopteris), which bear big petioles and show a concentric arrangement of meristematic structures, except in the medullar zone, where they adopt a spiral arrangement. The fronds are bipinnate, pinnules vary in size with an average of 5 mm.

From the ecophysiological viewpoint, the foliar remains are protected by thick cuticles, which is an infrequent feature in a fern. Another typical xerophytic adaptation is the presence of sunken stomata protected by two guard cells (Reymanówna, 1965).

Weichselia was a euohaline genus largely preadapted to terrestrial environments with high salt concentrations in coastal swampy zones mainly the pantropical

mangroves. This genus is frequently accompanied by conifers of the genus *Frenelopsis* (Álvarez-Ramis et al., 1992), leading to a typical association with comparable ecophysiological features to mangroves prevailing in the Tertiary

Apart from the morphological study of organic matter in ancient sediments, complementary chemical analyses by suitable destructive and non-destructive techniques are often used to establish the chemical signature (de Leeuw, 1988; Collinson et al., 1994; Hatcher and Clifford, 1997; Almendros et al., 1998, 1999; Lockheart, 2000; Otto and Simoneit, 2002). In the case under study, where microscopic inspection in addition to preliminary wet chemical treatments pointed to relatively high condensation and maturity degree (practical lack of free lipid, alkali-extractable humic fractions and poor yield from wet chemical degradation methods, suggesting a likely high degree of structural cross linking and covalent association between different original macromolecules) the research was carried out by employing techniques suitable to provide semiquantitative information when samples are processed as a whole. From this viewpoint, solid-state NMR spectroscopy and Curie-point pyrolysis are two valuable complementary analytical approaches widely used in organic geochemistry (Maciel and Sullivan, 1982; van Bergen et al., 1994b,c). These techniques can provide valuable semiquantitative information, even from condensed, insoluble macromolecular materials that cannot be completely isolated, without chemical alteration, from the mineral matrix. In particular, pyrolysis has been extensively used for the characterisation of organic sediments and kerogens because of its ability to release, apart from more or less diagnostic cleavage products, a series of thermoevaporation compounds with their original structures relatively unchanged, which can be readily removed from recalcitrant organic matrices (Hatcher and Clifford, 1997; Bosch et al., 1998).

2. Material

The Przenosza basement is located in an area under the riverine influence of tributaries to Vistula (Weichsel, in German) river, the paleoecological and sedimentological features with special emphasis on *Weichselia* genus being described by Reymanówna (1965). It includes organic matter forms with variable degrees of maturity. Thus, organic remains with well-preserved morphological features coexist with amorphous jet fragments

The material studied consisted of morphologically recognisable fragments of fronds (pinnules) collected from a carbonaceous layer made up predominantly of *Weichselia* remains. The remains were preserved either as large fronds with articulated pinnae or as small, dark-coloured pinnules and pinnae (Fig. 2). The layer also contained fragments of the corresponding stems and minor accompanying amounts of *Frenelopsis* sp.

3. Experimental

3.1. Preliminary analyses

To isolate the plant remains, fragments of the carbonaceous shale were disaggregated with water under a stereomicroscope. In the case of the samples used for examination under the light microscope, required for taxonomic identification, different concentrations of hydrogen peroxide were used to isolate a series of colourless fragments (Lesiak, 1994). For chemical analyses the mineral residues were isolated by physical methods, first using a lancet on the macroscopic remains on the rock (pinnae or

pinnules) then using sonication in water followed by treatments with 1% HCl-HF for 10 min at room temperature and centrifugation and washing with distilled water. These procedures provided sufficient amount (~500 mg) of material consisting of black friable fragments suitable for analytical purposes.

3.2. Solid-state ^{13}C NMR spectroscopy

The solid-state ^{13}C NMR spectrum was acquired with a Bruker MSL 100 spectrometer (2.3 Tesla) at 25.1 MHz and the CPMAS technique performed at 4 kHz. About one thousand free induction decays were accumulated for the spectrum. The pulse repetition rate was 5 s, and the contact time was 1 ms. The sweep width was 37.5 kHz and the acquisition time was adjusted to 0.016 s. The chemical shift range of the NMR spectrum was referred to tetramethylsilane (= 0 ppm). Under these conditions, it has been considered that ^{13}C NMR provides quantitative integration values in the different spectral regions (Fründ and Lüdemann, 1989).

3.3. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)

Analytical pyrolysis was performed with a Curie-point pyrolyser unit (Horizon Instruments) attached to a Varian Saturn 2000 GC-MS system. The sample was heated using ferromagnetic wires with a Curie-point temperature of 510 °C. The interface temperature of the pyrolysis unit was set at 250 °C and the pyrolysis time was 5 s. The injector, equipped with a liquid CO₂ cryogenic unit, was programmed from -30 °C (1

min) to 300 °C at 20 °C min⁻¹. In both cases the GC oven was programmed from 50 °C to 100 °C at a rate of 32 °C min⁻¹ and then up to 320 °C at 6 °C min⁻¹ for the ~55 min the total chromatographic run takes. For chromatographic separation a fused-silica capillary column (25 m × 0.32 mm) coated with CPSil 5 (film thickness 0.4 µm) supplied by Chrompack® The Netherlands and He as carrier gas were used. Compound identification was based on literature data and further comparisons with mass spectral libraries (Wiley, 1986; Nist, 1998). For semiquantitative measurement of the different chromatographic peaks, the sample was independently injected in a chromatograph with a flame ionisation detector under the same conditions; the data were expressed as relative abundances. Peaks representing less than 0.04 % were not taken into consideration.

4. Results

Microscopic examination of the plant cuticles under the light microscope confirms the identity of the macroremains, showing the typical frond morphology of *Paradoxopteris stromeri* Hirmer, which corresponds to the stem morphology of *Weichselia* described by Reymanówna (1965).

4.1. Solid state ¹³C NMR

The ¹³C NMR spectrum of the whole fossil plant remains (Fig. 3) is similar to that of a mature kerogen (Durand, 1980). As a whole, the spectrum practically lacks of typical

signals attributable to carbohydrate and oxygen-containing polyesters or protein and indicate, compared to fresh cuticular tissues from extant plants, a dramatic enrichment in aromatic carbons. These aromatic structures would probably have an important secondary origin, since if they were originated as results of a substantial enrichment of lignin, the spectrum should display in addition typical *O*-alkyl (45-110 ppm) signals, also characteristic of side-chain structures in lignin units. In fact, the spectrum is dominated by a major signal with apex at ~130 ppm, indicating aromatic or polyaromatic structures. The possible presence of heterosubstituted aromatic structures (shoulder at ~153 ppm) represents about a third part of the total ^{13}C NMR signal, which agrees with the occurrence and yields of series of similar structures in the pyrogram described below. The signal with maximum ~29 ppm is a typical indication of the presence of alkyl structures.

4.2. Curie-point pyrolysis

Figure 4a shows the total ion current of the pyrolysate of the whole kerogen and mass chromatograms revealing the major compound classes (alkanes, alkenes, alkylphenols, alkylbenzenes...). The overall compounds released suggest intense geochemical transformations of vascular plant remains with probable generation of newly formed structures. Aromatic series appear most abundant, as previously inferred from the NMR results.

The aliphatic series (around one third of total pyrolysis products) include $\text{C}_8\text{--C}_{25}$ alkanes and alkenes (Figs. 4b, 4c), with trace amounts of fatty acids (Figs. 4a, 4b). The distribution pattern of alkenes paralleled that of alkanes. The alkane series shows a bell-

shaped distribution with maximum at C₁₄ and no odd-to-even C number preference. This distribution pattern (i.e., homologous series of *n*-alkanes and additional unsaturated series composed of clusters of chromatographic peaks with molecular ions and mass spectrometric fragmentation patterns indicating *n*-alkenes and α,ω -alkadienes) has been interpreted (de Leeuw et al., 1991) as typical from pyrolytic cleavage of aliphatic macromolecules previously evidenced by ¹³C NMR, whereas there was no verification of a typical pattern of epicuticular lipids (long-chain alkanes with strong odd-to-even C preference number).

There were substantial amounts of phenols and alkylphenols (C₁–C₄), the assignment of which being relatively difficult because of the large number of isomers (in general methyl-substituted) (Fig. 4e). In fact, whereas *p*-cresol and *p*-ethylphenol (eluting in the two major peaks shown in the trace for phenols in Fig. 4e) are often considered to derive straightforwardly from lignins (Martin et al., 1979), the presence of other phenols alkylated at C1 and C2 positions is more frequent after pyrolysis of insoluble nonhydrolyzable sedimentary organic matter (Augris et al., 1998).

There was a series of relatively short- and *n*-chain alkylbenzenes (C₁–C₄) (i.e., mainly methyl substitutions in the benzene ring) judging from the mass spectra and the number of isomer compounds (Fig. 4d). Pyrolytic alkylbenzenes have been interpreted as being generated from the thermal cracking of dibenzofuran-like structures, or diaryl ethers, and these products are also considered as derived from condensation during coalification of phenols released during lignin degradation (Hartgers et al., 1995; Hatcher and Clifford, 1997).

A large number of pyrolytic aromatic products corresponded to polycyclic aromatic compounds, mainly alkylnaphthalenes (C₀–C₄), and anthracenes/phenanthrenes (C₀–C₃) and lower amounts of pyrenes (C₀–C₃) (Figs. 4f–4i). Hydroaromatic series were mainly

represented by fluorenes (C_0 – C_3) and some tetralins (Fig. 4h). The proportions of oxygen-containing aromatic products were negligible (only traces of catechols), and so were those of methoxyl-containing products: there were no appreciable amounts of typical lignin-derived methoxyphenols with vanillyl and syringyl-type structures or their methyl, ethyl, propenyl and vinyl derivatives (Boon, 1989), which is not surprising when it is assumed that demethoxylation occurs in the early dia- and catagenesis stages (Table 2).

5. Discussion

5.1. The origin of the condensed aromatic macromolecular material in the sediment

Pyrolysis data, similar to those of the Przenosza kerogen yielding no typical products related to biomacromolecules, have been described from most types of coalified structures where histological features remain intact, as it would correspond to the lack of substantial microbial attack (van Bergen et al., 1994a; van Bergen, 2001). Selective biodegradation alone cannot be invoked to justify the almost complete absence of *O*-alkyl and *O*-substituted aromatic structures, which are major constituents of lignocellulosic tissues. For instance, natural maceration in Carboniferous tree-fern cuticles indeed caused dramatic alteration in the proportions of the constituents of these plants, as reported by Zodrow and Mastalerz (2001), but in this case the IR spectroscopy revealed substantial amounts of alkyl and oxygenated structures, suggesting a much lower coalification degree than in the sample under study. Possible explanations of this virtual disagreement between histological and molecular data,

frequently observed in fossil plant remains, are: i) the drastic structural reworking of lignins and tannins, resulting in polyphenol macromolecules without significant disturbance of the general three-dimensional structure, and ii) a molecular-level replacement of the original biomacromolecules by incorporation of organic compounds, mostly aromatic, during fossilization (van Bergen et al., 1994b).

On the other hand, when considering the large number of peaks corresponding to aliphatic products (Fig. 4), pyrolysis results do not seem representative of the whole material as indicated by the ^{13}C NMR profile, as it could be the case with most aromatic structures as seen by NMR could not be pyrolysed due to highly condensed and thermally stable structure. Therefore, it seems reasonable to consider the above two hypotheses as well as the hypothesis that most of the aromatic structures could be formed from carbohydrate during diagenetic and/or thermal alteration of plant material. In fact, the NMR spectrum suggests much higher amounts of aromatic structures than those expected for the sole preferential removal of holocelluloses leading to the concomitant concentration of lignin, even assuming a substantial contribution of tannins (Abbott et al., 1998). In this sense, during thermal alteration of organic matter, such structures are believed to be transformed into aromatic rings or, probably into a continuous C–C or C–O–C three-dimensional network including newly-formed heterocyclic N-compounds (González-Vila and Almendros, 2003). This coincides with the observation of Lyons et al. (1995) who stated that a lignin-enriched structure was not a prerequisite for accumulation of a macromolecular aromatic network during coalification.

5.2. On the origin of the aliphatic chains in the macromolecule

The alkyl series in the pyrogram was similar to that obtained from other plant cuticles (Nip et al., 1986; Tegelaar et al., 1989). In fact, the above-indicated series (Fig. 4a) have been described as a typical signature of cutan structures, even in old sediments (e.g., Paleozoic), since it is considered that these plant constituents undergo little changes during coalification (van Bergen et al., 1994a,c).

The high diagenetic transformation of the cuticular material could also be inferred from the relative amounts of short-chain hydrocarbons. In the studied material the maximum in the alkyl series was at C₁₄ and the compounds >C₂₀ were in small amounts, which differs from the pattern described in recent *Agave* cutans, where the maximum occurs close to higher MW homologues (>C₂₀), and appreciable amounts of long chain compounds, as high as C₃₃, typical of cuticles from extant plants, were found. It has been suggested that thermal maturation of cutans is accompanied by the generation of lower molecular weight fragments of the biomacromolecule (Tegelaar et al., 1989; van Bergen, 1999).

6. Conclusions

In general, the transformation degree of the *Weichselia* remains in Przenosza Lower Cretaceous basement is extremely high when compared with more recent neighbouring Miocene deposits at Lipnica Mała (Fig. 1) described elsewhere by similar analytical techniques (Almendros et al., 1999). Pyrolysis of Lipnica Mała remains, mainly derived from *Glyptostrobus europaeus* showed small but well-defined methoxyphenol patterns accompanied by fatty acid series with maxima at C₁₆ and C₁₈ overlapped to alkane

series with maximum at C₂₃, that in this case could be interpreted as derived from selectively preserved epicuticular wax lipids.

On the other hand, our results resemble those reported by Edwards et al. (1997) from Devonian *Psilophyton*, where the presence of cuticular material was witnessed by the characteristic alkyl series but where methoxyphenols were absent and the occurrence of lignins was indirectly inferred from the alkylbenzene and alkylphenol patterns. What is more, the practical lack of catechols (Table 1) makes its composition different from that of Carboniferous fossil gymnosperms pyrolysed by Ewbank et al. (1996), where the occurrence of these compounds is still regarded as a result of lignin demethylation during early coalification stages, and could be considered an additional proof of the comparatively advanced maturation of the *Weichselia* remains from the Przenosza basement. Such results, which at first sight suggest intense demethoxylation due to active diagenetic processes and/or microbial reworking, are also consistent with the previous selective biodegradation of the lignocellulosic matrix leading to the accumulation of altered cuticular tissues.

In conclusion, the pyrolytic and NMR data suggest a typical kerogen from terrestrial material subjected to intense dia- and catagenetic transformations where most of the *O*-containing alkyl and/or aromatic compounds have been removed or transformed as it has also occurred with typical indicators for undegraded lignin and/or tannins, carbohydrate and protein. This points to extensive rearrangement of the original constituents into a newly formed condensed backbone. The waxes and carbohydrates, and probably most of the lignin and tannins, have been removed or incorporated into a kerogen matrix affected by severe reduction, aromatization and additional cross-linking reactions. In such material some evidence of doublets of alkenes and alkadienes persists

in the C₆–C₂₄ range with carbon preference index close to the unity, pointing to diagenetically transformed cutans.

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Table 1: Compounds released by flash pyrolysis of organic remains from Przenosza (Poland) Lower Cretaceous basement

MW	Compound	Relative abundance
92	Methylbenzene (toluene)	78.5
94	Phenol	12.4
106	C ₂ -Alkylbenzenes	83.2
108	Methylphenols (cresols)	13.1
116	Indene	6.3
118	Indane	5.7
120	Benzeneacetaldehyde	6.4
120	C ₃ -Alkylbenzene	100.0
122	C ₂ -Phenols (dimethylphenols + ethylphenol)	24.9
126	2(1 <i>H</i>)Pyridinone-1-ethyl	4.5
128	Naphthalene	18.4
132	Methylindanes	41.3
134	C ₄ -Alkylbenzene	35.1
136	C ₃ -Phenols	82.4
142	Methylnaphthalenes	20.0
148	C ₅ -Alkylbenzene	14.7
156	C ₂ -Naphthalenes	26.4
166	Fluorene	6.5
168	Dibenzofuran	4.2
170	C ₃ -Naphthalenes	4.1
176	C ₇ -Alkylbenzene	25.7
178	Anthracene	12.6
178	Phenanthrene	6.8
180	Methylfluorenes	1.0
182	Xanthene	2.7
184	C ₄ -Naphthalenes	1.6
192	Methylanthracene	6.1
194	C ₂ -Fluorenes	2.9
202	Pyrene	2.9
206	C ₂ -Phenanthrene	1.6
208	C ₃ -Fluorenes	2.6

Figure captions

Figure 1. Map of Poland and location of the Przenosza basement in Western Carpathians.

Figure 2. Pinnulae of *Weichselia reticulata* isolated from Przenosza Lower Cretaceous basement.

Figure 3. CP-MAS ^{13}C NMR spectrum of plant remains from Przenosza basement. Dashed lines indicate spectral ranges corresponding to the major C-types.

Figure 4. Total ion current and selected mass chromatograms of the pyrolysate (Curie-temperature: 510 °C) of *Weichselia*-derived kerogen from the Przenosza basement. The ions selected for plotting the different mass chromatograms are shown in parentheses. Icons on the uppermost total ion current plots correspond to those indicated for the different compound series.